Renewable and Sustainable Energy Reviews 29 (2014) 325–335

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Redox flow batteries for the storage of renewable energy: A review

Piergiorgio Alotto, Massimo Guarnieri*, Federico Moro

Dipartimento di Ingegneria Industriale, Università di Padova, via Gradenigo 6/A, Padua 35131, Italy

A R T I C L E   I N F O

Article history:
Received 1 August 2012
Received in revised form
29 July 2013
Accepted 11 August 2013
Available online 20 September 2013

Keywords:
Renewable energy
Energy storage
Electrochemical storage
Redox flow batteries
Vanadium flow batteries

A B S T R A C T

The need for grid-connected energy storage systems will grow worldwide in the next future due to the expansion of intermittent renewable energy sources and the inherent request for services of power quality and energy management. Electrochemical storage systems will be a solution of choice in many applications because of their localization flexibility, efficiency, scalability, and other appealing features. Among them redox flow batteries (RFBs) exhibit very high potential for several reasons, including power/energy independent sizing, high efficiency, room temperature operation, and extremely long charge/discharge cycle life. RFB technologies make use of different metal ion couples as reacting species. The best-researched and already commercially exploited types are all-vanadium redox batteries, but several research programs on other redox couples are underway in a number of countries. These programs aim at achieving major improvements resulting in more compact and cheaper systems, which can take the technology to a real breakthrough in stationary grid-connected applications.

Contents

* Corresponding author. Tel.: +39 3311727722; fax: +39 0498277524.
E-mail addresses: massimo.guarnieri@unipd.it, massimo.guarnieri@dii.unipd.it (M. Guarnieri).

1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2013.08.001

1. Introduction

For more than two hundred years the rapid development of industrial societies has relied on the exploitation of huge reserves of low-cost fossil energy. Resources formed over hundreds of millions of years have been burned in a relatively short time, with substantial environmental impact. Nowadays, electric energy demand exceeds 20×10^3 TWh/year and is growing at a rate of about 3% per year. Electrical energy is mainly produced in large fossil-fuel (approx. 2/3 of total), nuclear and hydroelectric power plants [1,2]. In the long term, this choice appears to be unsustainable. The growing demand for energy, particularly from large newly industrialized countries, and the increasing attention to environmental problems call not only for the optimal use of conventional sources, but also for their gradual replacement with environmentally-friendly renewable sources. Such policies, claimed for decades by scientists, have been finally embedded into the funding programs of central administrations in all industrialized countries.

Renewable sources, except hydropower, currently provide 4% of electricity production mainly from wind and solar energy, but their penetration is estimated to grow by more than 25% by 2030 [3].

Unlike conventional power plants, wind, solar, and other renewable sources are intermittent because they generate electrical power according to the time and climatic availability of the resources. Power variability ranges from the hourly time-scale related to the daily sun-light through the year, typical of photovoltaic (PV) systems, down to the min–s time-scale that is characteristic of wind generators.

The integration of primary energy sources with different features requires more attention in the design, control and management of the electric grid [4]. Traditional grids, which have not been designed to meet these goals, are often unable to provide satisfactory performance and recent studies have suggested that the grid can become unstable if power from these sources exceeds 20% of the whole generated power without adequate compensating measures, namely energy storage [5,6].

These issues call for complementing energy generation from renewable sources with energy storage systems capable of storing production surplus during some periods and of coping with higher demand in others [7–9].

Energy storage can also be useful in reducing electricity costs for distributors and consumers when electric companies apply policies of hourly pricing.

The use of energy storage on a large scale, both in a few large plants and in many small/medium size systems, allows to substantially limit the need of upgrading generating plants on the base of peak demand evolution, following instead a strategy of investment deferral.

Energy services can be basically grouped into two main categories, *power quality* and *energy management* (Fig. 1). The former refers to charge/discharge cycles on the short timescale (s–min) and includes sag compensation, power smoothing, grid stabilization, and frequency regulation. The latter concerns charge/discharge cycles on the long timescale (min–h), includes load leveling, load following, power balancing, peak shaving, and time shifting, and also contributes towards improving the grid load factor. *UPS* (uninterruptable power supply) is an energy storage service with intermediate features. Therefore, depending on the service, operating times range from the timescale of fractions of a second, with response times in the order of milliseconds, to several hours [10,11]. Moreover, power ranges from few kilowatt for domestic utilities to some gigawatt, for large plants.

Storage technologies capable of providing such performance will be essential parts of smart grids which are expected to spread in the near future. A recent authoritative report has forecasted investments exceeding $ 10 billions/year on energy storage technologies by 2020 [12].

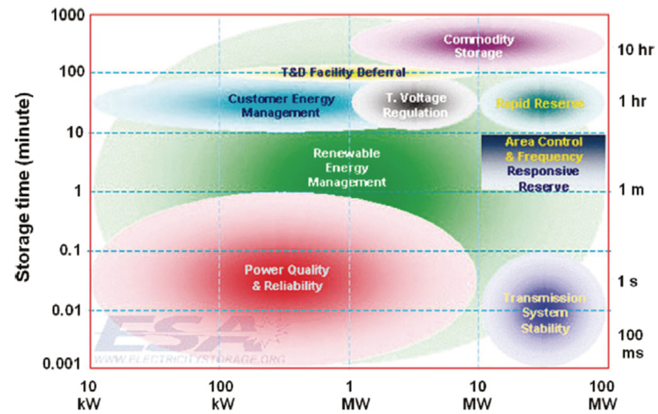


Fig. 1. Allocation of different energy storage requirements in the power—discharge duration diagram (*source*: Electricity Storage Association [13]).

2. Energy storage technologies

Economically convenient and technically competitive storage solutions must ensure not only response time and storage capacity suitable for meeting both the generation and grid needs, but must also show a long lifetime and be able to withstand a large number of charge/discharge cycles. Present-day technologies are characterized by different levels of development and are suitable for different storage and localization needs [14,15]. The best performing storage systems for electric energy applications are listed in Table 1 and described below, while design and operating features are reported in Table 2.

2.1. PHES (pumped hydro energy storage)

Hydro-pumped storage is by far the most exploited at present (127 GW of the total 128 GW worldwide storage capacity) [16]. Hydro-pumped plants operate efficiently when exceeding 20 MW and 50 MWh and top power reaches 3 GW at present (Bath County Pumped Storage Station, US-VA). However, they cannot respond to fast power demand, and are suitable for high-power long-time services, namely for energy managements [17,18]. Moreover, plants can only be sited in mountain regions with suitable differences in water levels, have an environmental impact, and are often threatened by long-term reservoir filling with sedimentary depositions. These drawbacks limit wider diffusion of PHES in several countries [19].

2.2. CAES (compressed air energy storage)

Compressed-air storage is suitable for large plants and is also prone to site issues. In fact, both large-scale existing plants are of the underground type, i.e. they store compressed air in huge underground caves. Huntorf, Germany, started in 1978 and rated 290 MW and 900 MWh, exploits two caverns of 310×10^3 m^3 at -655 to -800 m pressurized up to 66 bar [20]. McIntosh, US-AL, started in 1991 and rated 110 MW and 2800 MWh, uses a 560×10^3 m^3 cavern at -460 m pressurized up 74 bar [21]. In short, they cover similar energy management service as PHES. R&D activities, such as the ADELE project (200 MW, planned to be operational in 2013), are aimed at overcoming present limitations by resorting to an adiabatic operation (A-CAES, retaining the compression heat for reuse in the expansion phase [22]) in order to improve round-trip efficiency and by considering "aboveground" storage in tanks, even if all these solutions involve higher investment costs [23,24].

Table 1
Best performance and typical figures of main energy storage systems.

Technology	Top power [MW]	Top energy [MW h]	Energy density [W h/kg]	Discharge time	Response time	Round-trip efficiency	Cycle life $\times 10^3$	Capital cost [k$/kW]	Capital cost [$/kW h]	Capital cost [$/MW h/cycles]
PHES	3000	10^4	0.3	10^1 h	min	70–85%	20	0.4–5.6	10–350	0.5–3
CAES:										
Underground	300	10^3	10–30	10^0–10^1 h	min	60–	30	1.7	130–550	4–18
Aboveground	50	10^2	–	10^1 h	min	75%	> 10	2.2	430	43
TES	20	10^1	70	h	min	–	10	–	5,000	500
FES:										
Commercial	20	5	11–30	min	ms	85%	10^1–10^2	2.3	2,400	25–200
Lab	400	1	1.6	s	ms	–	–	–	–	–
SMES:										
Under development	100	10^1–10^3	–	min	ms	90–95%	10	2	> 10,000	1000
Lab	400	10	1.2	s	ms	–	–	–	–	–
EDLC	100	10^{-2}	10–30	s	ms	95%	500	–	4,600	10
ECES:										
Advanced lead-acid	10–40	10^0–10^1	25–50	10^0 h	ms	75–85%	3	4.6	130	150
Sodium-sulfur	34	10^1	150–120	10^0 h	s	85–90%	4.3–6	3.5	550	90–130
Sodium-nickel-chlorine[a]	1	6	95–120	10^0 h	s	85%	3–4	3.5	650	150–200
Lithium-ion	16	20	100–200	10^0 h	ms	95%	4–8	3–4	600	150–200
Electrolyzer/fuel cells	1	> 10	800–1300	> 10^0 h	ms	35–45%	50	17	> 10,000	200
Redox flow battery	2–100	6–120	10–50	10^0–10^1 h	ms	85%	> > 13	3.2	900	< < 70

–Means not applicable or unknown.
[a] Data courtesy of FIAMM S.p.A.—Zebra-Sonick (Italy).

Table 2
Design and operating features of main energy storage systems.

Technology	Scalability	Flexibility	W–W h Independency	Environmental impact	Safeness issue
PHES	Good	Low	Yes	High	High
CAES:					
Underground	Low	Low	Yes	High	High
Aboveground	Low	Low	Yes	Low	High
TES	Low	Low	Yes	Mild	Mild
FES:					
Commercial	High	Good	Yes	Low	Mild
Lab	Low	Low	Yes	Low	Mild
SMES:					
Under development	Good	Low	No	Low	Low
Lab	Good	Low	No	Low	Low
EDLC	Low	Low	No	Low	Mild
ECES:					
Advanced lead-acid	Good	Good	No	Low	Low
Sodium-sulfur	Good	Good	No	Low	Mild
Sodium-nickel-chlorine[a]	Good	Good	No	Low	Mild
Lithium-ion	High	Good	No	Low	Low
Electrolyzer/fuel cells	High	High	Yes	Low	Mild
Redox flow battery	High	High	Yes	Low	Low

[a] Data courtesy of FIAMM S.p.A.—Zebra-Sonick (Italy).

2.3. TES (thermal energy storage)

Thermal storage for grid applications is used in solar power towers for time shifting, i.e. for delaying the energy dispatch to a turbo-alternator and its conversion into electric energy [25]. High power, high energy, and slow response make them suitable for energy management services.

2.4. FES (flywheel energy storage)

Top power flywheel storage is incorporated into two generators installed at the JET (Joint European Torus) thermonuclear fusion experiment in England, each rated 400 MW/1 MWh, and the flywheel generator at Fusion Institute of JAEA (Japan Atomic Energy Agency) that stores 2.2 MWh [26]. Top commercial devices for grid applications are rated at lower power and higher energy, e.g. 20 MW and 5 MWh, achieved in a modular design based on 2 MW units and dedicated to UPS service [27]. They are capable of very fast response, but round-trip efficiency is high as far as discharge time is short and decreases at longer times due to friction effects, also in the case of electromagnetic bearings [28]. These features make them suitable for power quality services, such as frequency regulation. However, FESs for grid applications are still in a development phase and doubts remain on their final

commercial success. Flywheel storage is also being tested to assist regenerative breaking in electrical vehicles. FESs are affected by containment problems and gyroscopic effects from the Earth's rotation.

2.5. SMES (superconducting magnetic energy storage)

Superconductors require cryogenic cooling and are mainly used for producing high magnetic fields in magnetic resonance imaging (MRI) equipment and for lab devices, such as the windings of fusion research machines (e.g. non planar coils of the coming Wendelstein 7-X Stellarator [29], and poloidal solenoid and toroidal coils of the coming international nuclear fusion experimental tokamak ITER with $B=13.5$ T [30]). As regards grid applications, SMESs are suitable for fast operations, i.e. power quality services [31,32]. In fact, they are being designed for sag compensation and power quality assurance with top power around in the range from 10 to 1000 MW, which are expected to come ready by 2030–40 [33].

2.6. EDLC (electric double layer capacitor)

Electric double layer capacitors, namely super-capacitors, are used mainly to assist other power supplies in coping with surge power requirements particularly in electric/hybrid vehicles. The Shanghai municipality tested electric buses powered by super-capacitors (capabuses). Similarly to FES, round-trip efficiency is high as far as discharge time is short and decreases at longer times due to internal losses which tend to discharge the capacitors. Consequently, in grid applications EDLCs are used for fast services such as sag compensation [34,35]. Both SMESs and EDLCs are very expensive, even though EDLCs are virtually maintenance-free, while SMESs are almost servicing-free (the annual cost is estimated in 5% of the capital cost [32]). However, costs of EDLCs are steadily decreasing due to the market entry of new producers [36].

2.7. ECES (electrochemical energy storage)

All aforementioned storage technologies have specific features, each with its pros and cons. Among them, at present only PHES, CAES, and TES are suitable for long-time-scale (hours) grid energy storage. Conversely, FES, SMES, EDLC can operated at low and middle power and boast very fast response times, but are effective on the s–min timescale duration and are very expensive at present.

In this framework, several surveys show that electrochemical energy storage systems are the solution of choice for assisting intermittent renewable energy generators, e.g. PV and wind generators, with short- to long-time-scale energy storage, because of their site versatility, modularity that allows wide scalability, ease of operation, and static structure [37,38]. In fact, they are located in an area of the power/duration diagram out of the capabilities of other storage technologies (Fig. 2). They are expected to have wide implementation in the coming years as distributed storage systems and substantial funds have been already allocated for their scientific and technological development. Forecasts indicate a growth to 150 GW of installed power, corresponding to 10,000 times more than present capacity [10].

A specific feature of ECESs is that in most of them deep discharges strongly affect the battery life and consequently producers specify a depth of discharge (DOD) less then 100%, e.g. 80% or less, at which nominal cell lifespan is referred. Lifespan is the number of cycles for which the cell capacity (i.e. the deliverable charge) does not fall below a given fraction (e.g. 60%) of the nominal capacity (expressed in Ah). In practice, only a part of the

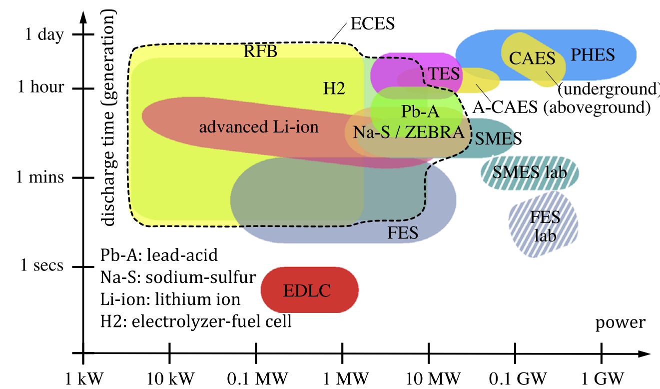


Fig. 2. Power-duration diagram of energy storage systems (plotted by this paper's authors.).

energy stored in most ECES device is usable and it is destined to decrease over time.

Another feature of most ECES, that is also shared with SMES and EDLC, is that the same device provides both power conversion and energy storage, that allows for very compact systems, but, at the same time, bonds power to energy sizing.

3. Redox flow batteries

Among electrochemical systems, redox flow batteries (RFBs) represent one of the most recent technologies and a highly promising choice for stationary energy storage [39,40]. They are electrochemical energy conversion devices, which exploit redox processes of species in solution in fluid form, stored in external tanks and introduced into the RFB when needed. In this sense a RFB is similar to a polymer electrolyte membrane fuel cell (PEMFC) and indeed it is a sort of FC. The most appealing features of this technology are: scalability and flexibility, independent sizing of power and energy, high round-trip efficiency, high DOD, long durability, fast responsiveness, and reduced environmental impact [41]. Such features allow for wide ranges of operational powers and discharge times, making them ideal for assisting electricity generation from renewable sources (Fig. 2).

RFB are presented in the following sections. First their structure and principle of operation are described, indicating their pros and cons. Then, an historical overlook of early RFBs is followed by a report of most used and studied types. The state of the art of the most important plants put into service and the developments programs is then presented, followed by the most important research issues.

3.1. RFB main features

The principle behind a RFB cell is a couple of electrochemical reduction and oxidation reactions occurring in two liquid electrolytes (with typical concentrations of $1 \div 5$ M) containing metal ions ($0.1 \div 9$ M, strongly depending on the chemistry used) [42]. The reduction half-reaction at one electrode extracts electrons and ions from one electrolyte, while the oxidation half-reaction at the other electrode recombines them into the other electrolyte (Fig. 3). Ions migrate from one electrode to the other (from anode to cathode) through an electrolyte that is impermeable to electrons, which are thus forced through an external circuit providing electric energy exchange. In order to keep the solutions in the liquid phase, the cell must operate at near room temperature, for which the ion-conducting electrolyte of choice to be placed between the two electrodes is a polymeric membrane. Both half-

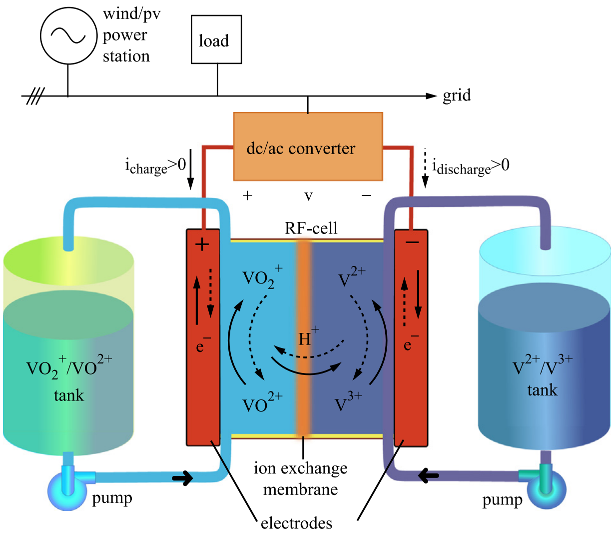


Fig. 3. Diagram of a RFB energy storage system: RFB stack and electrolyte tanks are separated.

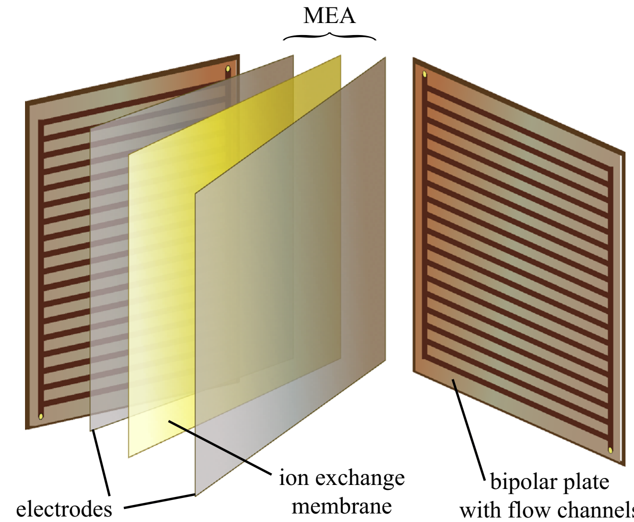


Fig. 4. Diagram of a RFB cell with MEA (membrane-electrode assembly) elements and bipolar plates with parallel-channel layout for flow-by distribution.

cells are connected to external storage tanks providing the needed volume of electrolyte solutions circulated by pumps.

3.2. Pros

Compared to other electrochemical storage technologies, in RFBs, as well as in FCs, power conversion is separated from energy storage, thus allowing for independent power and energy sizing. This feature allows for virtually unlimited capacity simply by using larger storage tanks. Practically speaking, energy of present designs spans from 10^2 to 10^7 Wh, a range exceeding that of most ECES at least by one order of magnitude. RFBs and FCs have more advantages than other electrochemical devices when storage times longer than 4–6 h are required.

Likewise PEMFCs, the electrochemical heart of RFBs is the MEA (membrane electrode assembly), a sandwich consisting of two catalyzed electrodes with an interposed polymeric membrane (Fig. 4). In order to allow electrolyte flow toward the electro-active sites, the electrodes have a porous structure that can be obtained with carbon base materials such as carbon felt, carbon-fiber paper, or carbon nanotubes. These allow for porosity in the order of 0.8, thereby achieving a compromise between good electrode permeability and high electrode active area [41].

However, major differences exist. An FC-based storage system usually resorts to two different converters: the FC itself for generating electricity and an electrolyzer for storing energy by converting water into hydrogen and oxygen by means of electricity. Instead, RFB reactions are completely reversible, enabling the same cell to operate as converter of electricity into chemical energy and vice-versa. RFBs operate by changing the metal ion valence, without consuming ion metals, thereby allowing for long cycle service life. Moreover, managing gases such as hydrogen in FCs is far more problematic than handling and storing RFB's liquid electrolytes, which can be kept inside two low-cost tanks. Only two pumps are needed in RFBs for circulating the electrolytes between the tanks and the cell electrodes.

Cell temperature can be easily controlled by regulating the electrolyte flow, allowing to operate the cells in the optimal conditions, e.g. at maximum efficiency [43]. The SOC (state of charge) can be easily monitored through the cell voltage while very deep discharges are viable which do not affect the cell morphology. No self-discharge occurs because the two electrolytes are stored in different tanks, and cells can be left completely discharged for long periods with no ill effects.

RFBs are capable of rapid response that allows them to span from power quality to energy management services. They can be overloaded over a short period. Moreover, rapid refueling by solution exchange is possible, in case of need, and furthermore, they require low maintenance.

3.3. Cons

The power density and energy density of RFBs are low compared to other technologies, making them unsuitable for mobile applications at present. Accordingly, cell active areas and membranes are quite large, increasing the dimensions of the battery and causing high transverse gradients of the solutions flowing toward the sites of electrochemical activity inside the electrodes. Consequently, this reduces the average current density and nominal current with respect to the maximum theoretical values, achievable with uniform maximum current density.

Since electrolytes are conductive, they are prone to shunt currents, i.e. electric currents along the distribution and flow channels, which produce additional losses and affect electric efficiency. A careful control of the electrolyte temperature is required to avoid solution precipitation below 15 °C and above 35 °C. This calls for heat/temperature control by means of specifically designed systems.

4. Historical overlook

The vanadium (V) redox couple was first mentioned in a 1933 patent by P.A. Pissoort, in France (Patent 754 065—1933) and a patent on a titanium chloride flow cell was registered by Walter Kango in Germany in 1954 [44].

Early systematic studies were undertaken in the 1970s within NASA's space programs by Thaller [45,46,47], starting with Fe–Ti electrolytes [48]. These research programs included the investigation of other redox couples including Fe–Cr [49]. This NASA program was brought to a close in 1984 [50].

Around 1980 in Japan interest grew as regards electrochemical storage intended for complementing pumped hydro. Research took place within the Moonlight Project of the New Energy and Industrial Technology Development Organization (NEDO). In this framework Fe–Cr redox systems in hydrochloric acid solution were investigated at the Electrotechnical Lab (ETL) in Japan [51].

The vanadium idea was revived in 1978 in Italy by A. Pelligri and P.M. Spaziante (GB Patent 2030349—1978), but without significant development. The first known successful demonstration and commercial development of redox flow batteries employing vanadium in each half cell (VRB, Vanadium/vanadium Redox Battery) was carried out at the University of New South Wells (UNSW), AU, by Skyllas-Kazacos, who registered a patented in 1986 (AU Patent 575247—1986) [52–54]. At that time the interest in vanadium in Australia was enhanced by new mining programs aimed at catapulting the country to a leading position among vanadium producers worldwide (nowadays top producers are China, South Africa and Russia).

Subsequently, a new technology was developed in Japan to obtain vanadium as a byproduct of crude oil refineries and from soot of heavy fuels, and later from titanium production. These achievements drew Japanese attention to the exploitation of vanadium. Around 1989 R&D was boosted on VRB, taking advantage of Fe–Cr know-how. Early test systems appeared in 1996–2000 and commercial installations started in 2001.

In the last decade more attention has been focused on RFB systems and more producers have appeared in different countries, as discussed below. Present applications are not limited to load leveling and power stabilization of intermittent renewable sources, since VRBs have been successfully tested in voltage sag compensation and as sources of emergency power supply [55,56]. To a minor extent Zn–Br_2 and Br–polysulfide systems are also under development.

5. Present RFB technologies

5.1. Fe–Cr system

After NASA's initial research, Fe–Cr test systems in the range of 10–60 kW were produced in Japan by Mitsui Engineering and Shipbuilding Co. Ltd, Kansai Electric Power Co. Inc, and Sumitomo Electric Industries Ltd in the years 1984–1989. They exploit the following redox reaction [40,42].

positive electrode

$$Fe^{2+} - e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Fe^{3+}$$

negative electrode

$$Cr^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cr^{2+} \tag{1}$$

The open circuit voltage (OCV) of a Fe–Cr cell is 1 V. The drawbacks of this cell include slow reaction of the Cr ion, membrane aging, and cell degradation due to the mixing of the two ions, and low energy density. These features make them inferior to VRBs, to the extent that they were abandoned in favor of other redox couples.

5.2. VRB system

Among various RFB metal ion combinations (zinc–bromine, zinc–cerium, magnesium–vanadium, vanadium–cerium, vanadium–polyhalide,...), the most researched and successful technology is the VRB, the only technology that has reached effective commercial fruition [57]. It uses vanadium/vanadium dissolved in aqueous sulfuric acid (~5 M). An advantage is that by using the same metal ions in both electrolytes, the electrodes and membrane are not cross-contaminated and the cell capacity does not decrease with time, allowing for a longer lifespan.

However, some differences in the metal ion charge oxidations at the two electrodes must exist, so that vanadium IV–V (tetravalent–pentavalent) is used on one side and vanadium II–III (bivalent–trivalent) on the other, thereby exploiting the ability of this element to exist in solution in four different oxidation states. Electrochemical half-reactions of a VRB are as follows.

positive electrode

$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + 2H^+ + e^-$$

negative electrode

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \tag{2}$$

During charging at the positive electrode tetravalent vanadium within VO^{2+} ions is oxidized to pentavalent vanadium within $VO_2{}^+$ ions, while at the negative electrode trivalent ions V^{3+} are reduced to bivalent ions V^{2+}. The hydrogen ions $2H^+$ move through the membrane to maintain the electrical neutrality of the electrolytes. The standard OCV of a VRB cell is $E^o = 1.26$ V at 25 °C, but in fact real cells exhibit $E^o = 1.4$ V due to the correcting Nernst's factors.

VRBs exhibit a current density in the order of 50–80 mA/cm^2 and correspondingly a power density barely reaching 0.1 W/cm^2, which is much lower than that of equivalent PEMFCs. Stored energy density does not exceed 25–35 Wh/L. Active cell areas in the order of 6000 cm^2 and over are needed for managing currents of some hundreds of amperes in a single cell.

5.3. V–Br cell

Improved performance has been obtained in the last years using vanadium–bromine (V–Br) dissolved in a solution of hydrogen chloride (1.5–2 M), which are based on the following redox reactions.

positive electrode

$$2Br^- + Cl^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Cl\,Br_2{}^- + 2e^-$$

negative electrode

$$2V\,Br_3 + 2e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2V\,Br_2 + 2Br^- \tag{3}$$

They are capable of $E^o = 1.3$ V and a 35–70 W h/L energy density, but have additional problems due to the potential production of hazardous bromine vapors [58].

5.4. V–O_2 cell (VOFC)

Another promising approach for improving the energy density of VRBs and saving on raw materials consists in the hybrid vanadium–oxygen redox fuel cell (VOFC) that replaces the positive half-cell electrolyte and electrode with air according to the following reactions.

positive electrode

$$2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 4H^+ + O_2 + 4e^-$$

negative electrode

$$4V^{3+} + 4e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 4V^{2+} \tag{4}$$

The OCV is about $E^o = 1$ V. In fact, one electrolyte sub-system is saved, which roughly doubles the energy density. The concept was patented by Kaneko et al.[59] and investigated by Menictas and Skyllas-Kazacos from 1997, with research still ongoing [57,60].

5.5. Load operation

Similarly to other electrochemical devices, a VRB cell exhibits an activation overpotential η at each electrode when converting energy.

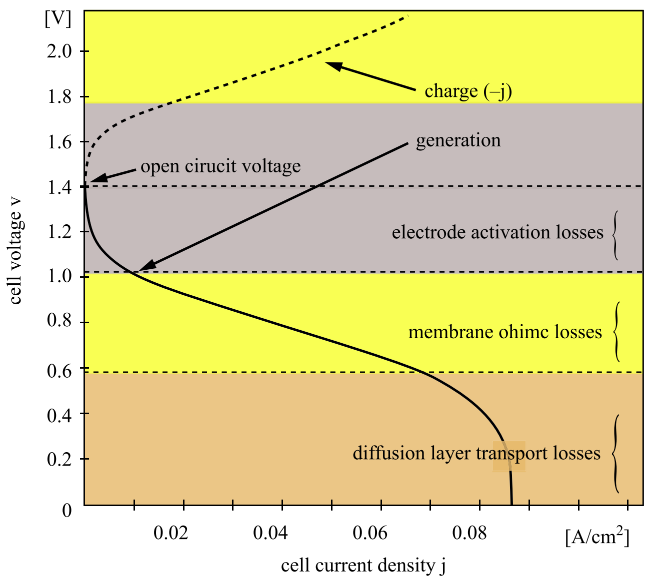


Fig. 5. Polarization curve of a RFB in the electrical generation region (first quadrant) and charge region (second quadrant reversed on the first one).

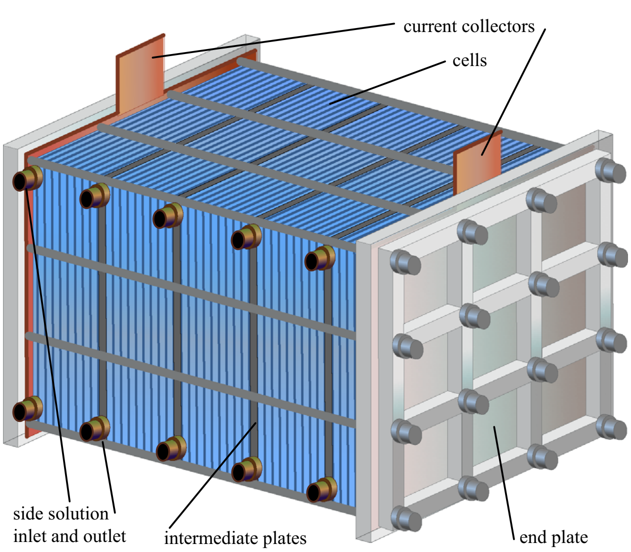


Fig. 6. RFB stack with side fluid feedings—series of about 100 cells with active areas as large as 0.4 × 0.4 m are usual.

According to Butler–Volmer's equation these overpotentials are related to the cell current density j as:

$$j = j_o \left[\frac{c_r(0,t)}{c_r^*} \exp\left(\frac{\alpha F}{RT} \eta \right) - \frac{c_p(0,t)}{c_p^*} \exp\left(\frac{(1-\alpha)F}{RT} \eta \right) \right] \quad (5)$$

where j_o is the exchange current density, c_i are the species concentrations of the reagents and products indicated in (2) ($i=r$ regents, $i=p$ products) at the electrochemical activity sites, α is the transfer coefficient (about 0.5), F the Faraday constant, R the gas constant, and T the absolute temperature. The c_i/c_i^* ratios express the dynamically reduced concentrations $c_i(0,t)$ normalized to the steady-state equilibrium values c_i^*.

Overpotentials make the load voltage v different from OCV E^o as $v = E^o - \eta$. The voltage is higher than E^oin the charge phase, when $j < 0$ and electric power enters the cell, and lower in the generation phase, when $j > 0$ and electric power is released.

The exchange current density j_o is a crucial parameter: the higher the j_o, the lower the η for a given j, thus improving performance and round-trip efficiency. Activation overpotentials are the main culprits of cell internal losses at lower current densities (i.e. with $c_i/c_i^* \cong 1$). j_o depends on the electrochemical reaction and electrode structure. Technical solutions for increasing it consist in high concentrations, lower activation barriers (i.e. higher activity provided by efficient catalysts based on noble metals), and a larger active area, achievable with highly porous electrodes (e.g. nanostructured materials).

The material of choice for the electrode-separating electrolytic membrane is a perfluorosulfonic acid polymer, patented as Nafion by DuPont, capable of allowing ion transport by binding cations to its sulfonic acid sites when properly hydrated. At mid current density the internal losses are dominated by the resistive behavior of the ion conducting membrane (Fig. 5). It behaves like a linear resistance, at constant temperature and hydration.

Higher current densities are dominated by transport losses in the electrode diffusion layers due to a dramatic reduction of the concentrations ($c_i/c_i^* \ll 1$). They cause the cell voltage to collapse as the current density approaches its limit value.

Since the voltage of a single RFB cell is around 1.5 V at its highest, more cells are connected in series and assembled into stacks to achieve higher voltages (Fig. 6). Resembling a design typical of fuel cells, bipolar plates are used to connect one cell to the other (Fig. 4). Two methods are used for feeding the cells along the stack as uniformly as possible with the two electrolytic solutions. In the "flow-by" design bipolar plates are provided with flow channels, which allow the electrolytic solutions to be distributed along transverse planes from where they percolate longitudinally into the electrode diffusion layers towards the

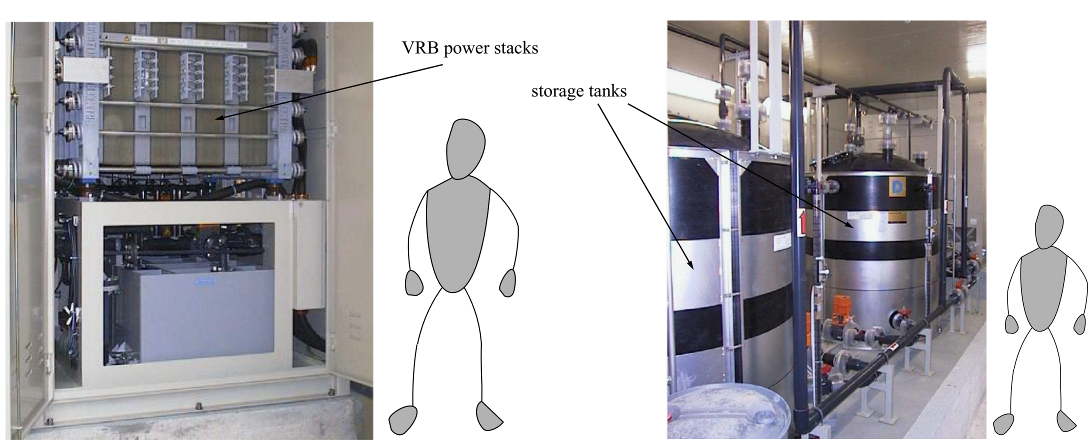


Fig. 7. Power (left) and energy (left) components of a SEI VRB system rated 125 V, 500 A, 45 kW, 90 kWh. The stack (left top) consists of 100 cells in series. The two tanks (right) are sized 5 m^3 and store 4000 L. (courtesy of RSE SpA, Milan, Italy.).

electroactive sites. In the "flow-through" design no flow channels are provided in the bipolar plates and the electrolytic solutions percolate transversally from the side into thicker electrode diffusion layers.

The response time, dependent on the dynamics of the electrochemical activity, is very fast, even less than one millisecond. Properly designed RFB stack systems can respond immediately to surge power demand and provide sag compensation and UPS service with no need for an auxiliary high power/low energy storage system. Tests have shown response times less than 0.5 ms for a 100% load increase and overload tolerability up to 400% for 10 s. It must be noted, however, that much longer overloads can cause electrode delamination.

Since the vanadium ions of a VRB are dissolved sulfuric acidic solution, the materials in contact with the electrolytes, including tanks and pumps, must be resistant to corrosion. Polyethylene and rubber are usually adopted for this purpose.

The load-voltage dependence shown in Fig. 5, which is typical of electrochemical devices, calls for conditioning of the output electrical power by means of an electronic power management unit able to ensure a load voltage independent of the load current. In the case of grid-connected systems, power management also includes a DC/AC and AC/DC converter. The proper design of such converter grants the system high round-trip efficiency.

Low power density and energy density make present RFB unsuitable for mobile uses, but exploitable in stationary applications. The systems already put into operation have demonstrated a very long working life: up to 270,000 charge/discharge cycles have been attained. Present costs are in the order of 600 €/kW and 60–100 €/kWh, and Nafion used for cell membranes is the most expensive material required in VRBs. A typical 45 kW / 90 kWh VRB system is shown in Fig. 7.

The previous presentation indicates that the design of a RFB storage system requires a broad expertise in the fields of electrochemistry, chemistry, chemical engineering, electrical engineering, power electronics, and control engineering.

6. State of the art of Rfbs

6.1. Main VRB plants installed

Some of the major plants ever built based on VRB technology are reported hereafter in chronological order.

- 1996: 200 kW/800 kWh installed by Mitsubishi Chemicals at Kashima-Kita Electric Power, Japan, for load-leveling [61].
- 1996: 450 kW/900 kWh installed by Sumitomo Electric Industries (SEI) at Tasumi Sub-Station, Kansai Electric, Japan, for peak shaving.
- 2000: 200 kW/1.6 MWh installed by SEI at Kansai Electric, Japan, for peak shaving.
- 2001: 170 kW/1 MW installed by SEI at Hokkaido Electric Power Wind farm, Japan, for wind turbine output power stabilization.
- 2001: 1.5 MW/1.5 MWh installed by SEI in a semiconductor fabrication plant at Tottori Sanyo Electric, Japan, for peak shaving and emergency back-up power [56].
- 2001: 250 kW/500 kWh installed by VRB Power at Stellenbosch University for ESKOM Power Corporation, South Africa, for peak shaving and UPS back-up power.
- 2001: 500 kW/5 MWh installed by SEI at Gwansei Gakuin University, Japan, for peak shaving.
- 2001: 45 kW/90 kWh installed by SEI at CESI, Milan, Italy, for R&D about distributed power systems (Fig. 7).
- 2003: 500 kW/2 MWh installed by SEI in a High-Tech factory in Japan for UPS/peak shaving [56].
- 2003: 250 kW/1 MWh installed by Pinnacle VRB for Hydro Tasmania at Huxley Hill Wind Farm on King Island for wind energy storage and diesel fuel replacement [55].
- 2004: 250 kW/2 MWh installed for PacificCorp by VRB Power at Castle Valley, Moab, US-UT, for voltage support and rural feeder augmentation [9].
- 2005: 4 MW/6 MWh installed by SEI for Electric Power Development Co, Ltd in Tomamae, Hokkaido, Japan, for wind energy storage and wind power stabilization [62].
- 2010: 100 kWh made of 18 kW stacks in Vierakker, The Netherlands, by Cellstrom GmbH, Austria.

6.2. Worldwide development programs

The 4 MW/6 MWh plant installed by SEI for J-Power in 2005 is the largest VRB plant built so far. It withstands a temporary overload of up to 6 MW and is intended for smoothing power output fluctuations at Subaru Wind Villa Power Plant, rated at 30.6 MW. The system consists of 4 banks, each made of 24 stacks and rated 1 MW (maximum 1.5 MW). Each stack consists of 108 cells, with a rated power of 45 kW. Over 3 years of operation it completed more than 270,000 cycles.

Systems like this one have demonstrated very good performance in smoothing and leveling the fluctuating power generated by wind generators. Most of them have been built by SEI of Japan and VRB Power Inc., based in Vancouver, who in around 2005 bought SEI patents. In 2009 all VRB assets of VRB Power where acquired by Prudent Energy, based in China, in a plan of expansion in China and abroad. The company recently announced its decision to invest $ 29.5 million for boosting production. Also the Dalian Institute of Chemical Physics, the Chinese Academy of Science, and Chengde Wanlitong Industrial Group are developing RFB technologies in China [63]. The reason for this interest can be found in Chinese plans to expand the exploitation of intermittent renewable energy sources. Wind power produced in the country is expected to rise from about 20 GW in 2010 to 100 GW in 2015 and about 300 billion Yuan ($47.2 billion) per year will be invested in power grid improvements over the next decade to handle it.

Other Asian countries have undertaken enthusiastic developments. Cellennium Company Ltd. of Thailand produces licensed VRB systems while Samsung Electronics Co. Ltd. in South Korea is developing RFBs with non-aqueous electrolytes.

In Australia V-Fuel Pty Ltd., formed in 2005 by M. Skyllas-Kazacos and M. Kazacos, is pursuing further development in V–Br technology in cooperation with UNSW. Other Australian companies working on RFB, are ZBB Energy Corp. and Redflow Ltd., both engaged in developing and installing Zn/Br_2 batteries.

In the United States the DoE launched a program on RFB that entrusted Ashlawn Energy, LLC to design a VRB test plant rated at 1 MW/8 MWh and Primus Power Corp. was funded to develop a 25 MW/75 MWh system based on Zn/Cl_2 RFB. Premium Power Corp. is developing Zn/Br_2 batteries.

In Europe Renewable Energy Dynamics (RED-T), Ireland, Cellstrom GmbH, Austria, RE-Fuel Technology Ltd., UK, are developing and producing VRB systems. High-energy density RFBs are being investigated in the UK by Plurion Ltd that is working on Zn–Ce systems. In Germany, the Fraunhofer-Gesselschaft is starting a research program on non-aqueous electrolytes and has designed a VRB system to be used as a benchmark that consists of eight modules of seven 100-cell stacks capable of 2 kV, 1 kA, 2 MW output, provided with two tanks of 300 m^3 for storing 20 MWh to be contained in a building of 35×17 m [64] (Fig. 8).

These R&D and industrial interests prove that the RFB market is expected to grow significantly in the future, as smart grid technologies will expand worldwide.

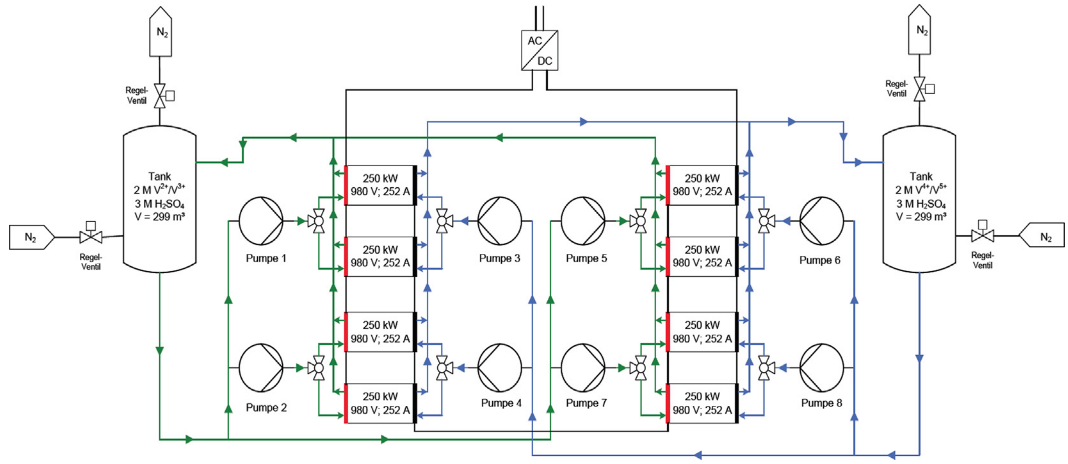


Fig. 8. Schematic of the 2 MW/20 MWh VRB project to be used at Frauhofer as a benchmark for advanced non-aqueous RFBs (courtesy of Fraunhofer-Gesselschaft, Germany.).

7. Research issues

The RFB technology has not yet achieved a real breakthrough and R&D programs are required to reach full commercial potential [65]. Next-generation more competitive systems, expected in 5 years, will be able to provide the capital and cycle life cost reductions that are essential for widespread commercial success.

Research is ongoing to achieve an in-depth knowledge of the fundamental RFB processes, as regards electrochemical reactions at the electrode surfaces [66,67], complex charge transport [68,69] and non-idealities in the RFB couples and electrolytes, species charge transport and crossover in ion-exchange membranes, fluid mechanics and transport of electrolyte through the electrodes, aimed at determining optimal electrode structures and properties [41,42].

More compact systems exhibiting higher power and energy densities will resort to non-aqueous electrolytic solutions and/or to improved electrode activity.

Improved electrolytes can expand the operation temperature range and nanostructured electrodes promise to achieve an increased effective electroactive surface area and hence an improved exchange current density j_o.

New experimental VRB cells have already exhibited current and power densities much higher than presently commercialized systems, indicating that even better performance will be achieved in optimized devices [70,71]. The best technologies for powering electric cars are currently nickel–metal–hydride and lithium-ion or lithium-polymer, which can boast power densities as high as 120–200 Wh/kg. Although present-day commercial RFBs, with their modest 30–50 Wh/kg, are unsuitable for such use, the aforementioned improvements are promising also in this direction. In the next future, more compact and more flexible RFB systems, provided with high power and energy densities, are expected to be competitive for powering electric vehicles. Thanks to their intrinsic power-energy independence they could allow for greater range, thus overcoming one of the major drawbacks that burden present-day electric cars, typically ranging around 100 km.

Significant cost reductions are expected from new ion conducting materials for the cell membrane, which can replace the expensive Nafion and produce at the same time reduced cell ohmic losses [72,73]. Incidentally, material cost reduction will also be provided by higher power density thanks to more compact designs.

Engineering efforts are addressed at system scale-up and structural and operational optimization concerning flow geometries, state-of-charge monitoring and supervisor systems. In fact, present RFB systems are far from optimal. Numerical modeling and simulation are instrumental to these targets. Multi-scale, multidimensional, multi-physical, steady-state and dynamic models are under development to simulate accurately the behavior of cells, stacks and systems. The modeling problems are similar to those posed by DAFCs (direct alcohol fuel cells) which also make use of MEAs, bipolar plates, and stacks and are also fed with liquid solutions instead of gases. Numerical tools developed in that field can be used to simulate the behavior of RFB systems [74]. Sophisticated modeling tools are aimed at developing advanced bipolar plates with either flow-by or flow-through diffusion of the electrolytic solutions [75]. In this case the aim is to minimize transverse concentration gradients and at the same time reduce electrolyte electrical conductance, thereby lowering shunt currents [76]. Innovative computational techniques are required to cope with the highly challenging numerical problems arising from cell elements with multi-physic non-linear material behavior and high aspect ratio geometries [77,78]. At the same time, advanced control systems will provide automatic electrolyte rebalancing and capacity correction. They may allow the remote operation of large RFB systems. Electrolyte flow-rates strongly affect cell performance (i.e. v–i polarization curve) and at the same time pumping power is one of the main factors affecting overall efficiency. Ongoing technological development are aimed at design optimization of the distribution channels, also by means of computational modeling, so as to provide high mass transfer coefficients with low pressure drop. Operational optimization of flow-rates will also contribute to ensure reduced pumping power while preserving electric performance [79].

As far as the electrical interface of RFB systems is concerned, modeling, simulation, and optimization are aimed at designing supervisor and control sub-systems with proper feed-back loops and optimized response times. These are essential for ensuring improved performance as regards peak shaving, sag compensation and load leveling, in the context of smart-grids operations. Flexible solutions for interfacing both the DC intermittent renewable energy sources and AC grid and load can be obtained with DC/DC converters coupled to two quadrant inverters. Proper topologies of the converter must be selected in order to achieve optimal operating conditions of the RFB stacks [80]. Non-linear control techniques of the inverter can allow RFB systems to provide active and reactive power to the smart-grid connected loads. Adaptive multi-variable control techniques are aimed at keeping the RFBs in optimal operating modes. Success in designing such power management sub-systems, including both the DC/DC converter and the inverter, strongly hinges on the accuracy of modeling the whole system. To achieve this target, lumped model approaches are the tools of choice, which can be interfaced with optimization procedures.

Optimal solutions will also take into account economical aspects (operating earnings and savings arising from the RFBs operation) and environmental aspects (primary energy savings, carbon dioxide savings). The results of these analyses will make it possible to assess the viability of operation of RFBs within the context of energy hubs. These development programs are strongly interdisciplinary and call for collaborative programs among researchers with different expertise. The present scientific challenge raised by RFBs consists in the implementation of low cost, high efficiency and long lifetime solutions, suitable for large-scale industrial exploitation in competitive energy storage devices able to overcome the limitations that hamper other conventional systems.

Research programs currently underway aim at reducing the cost and size of VRB systems to make them commercially competitive [65]. A reasonable medium-term target is to halve cost per unit of power and increase by several times the power density. Many laboratories are developing research programs on these issues, not only in Australia, China, Japan, US, Ireland, Austria, UK, and Germany, as already stated, but also in Singapore, Korea, Canada, Spain, and other countries are next to do so. More than 100 papers have been published in indexed scientific journals in the first six months of 2013.

8. Conclusions

RFBs are a promising energy storage technology. First-generation systems, based on the all-vanadium VRB technology, have already been successfully demonstrated in test plants and their commercial exploitation is ongoing. Second-generation systems, with improved power and energy densities, are under technical development, but further development in electrochemical materials and systems engineering is expected to produce third-generation systems capable of achieving a technical and commercial breakthrough in smart-grid-oriented applications. These systems will support intermittent renewable energy sources, where they can enable a variety of advanced operations on a wide range of timescale, including sag compensation, power smoothing, UPS, load leveling, load following, power balancing, peak shaving, and time shifting, with major technical and economical benefits. Future high-density systems are also expected to be suitable for powering electric vehicles.

References

[1] World Energy Outlook 2011, International Energy Agency; 2011. ⟨http://www.worldenergyoutlook.org⟩.
[2] Annual Energy Outlook 2012 Early Release Overview, U.S. Energy Information Administration; 2012, ⟨http://www.eia.gov/forecasts/aeo/er⟩.
[3] European Commission, Proposal for a COUNCIL DECISION establishing the Specific Programme Implementing Horizon 2020—The Framework Programme for Research and Innovation (2014–2020), COM(2011) 811 final, 2011/0402 (CNS).
[4] Coster E, Myrzik J, Kruimer B, Kling W. Integration issues of distributed generation in distribution grids. Proceedings of the IEEE 2011;99(1):28–39.
[5] Swierczynski M, Teodorescu R, Rasmussen CN, Rodriguez P, Vikelgaard H. Overview of the energy storage systems for wind power integration enhancement. In: Proceedings of the IEEE international symposium on industrial electronics (ISIE 2010), 3749-3756, 2010.
[6] Vazquez S, Lukic S, Galvan E, Franquelo LG, Carrasco JM, Leon JI. Recent advances on energy storage systems. In: Proceedings of the IECON 2011: 37th annual conference of the IEEE industrial electronics society , 4636-4640, 2011.
[7] Kondoh J, Ishii I, Yamaguchi H, Murata A, Otani K, Sakuta K, Higuchi N, Sekine S, Kamimoto M. Electrical energy storage systems for energy networks. Energy Conversion and Management 2000;41(17):1863–74.
[8] Roberts BP, Sandberg C. The role of energy storage in development of smart grids,. Proceedings of the IEEE 2011;99(6):1139–44.
[9] Hennessy T. DOE energy storage systems research program, annual peer review, Washington DC; 3 November 2006.
[10] Ren L, Tang Y, Shi J, Dou J, Zhou S, Jin T. Techno-economic evaluation of hybrid energy storage technologies for a solar-wind generation system. Physica C: Superconductivity 2013;484:272–5.
[11] Zahedi A. Maximizing solar PV energy penetration using energy storage technology. Renewable and Sustainable Energy Reviews 2011;15:866–70.
[12] Pieper C, Rubel H. Revisiting energy storage. There is a business case Boston consulting group report, February 2011.
[13] ⟨http://www.electricitystorage.org/technology/tech_archive/technology_comparisons⟩.
[14] Pickard WF, Shen AQ, Hansing NJ. Parking the power: strategies and physical limitations for bulk energy storage in supply-demand matching on a grid whose input power is provided by intermittent sources. Renewable and Sustainable Energy Reviews 2009;13:1934–45.
[15] Kaldellis J, Zafirakis D, Kavadias K. Techno-economic comparison of energy storage systems for island autonomous electrical networks. Renewable and Sustainable Energy Reviews 2009;13:378–92.
[16] Yang CJ, Jackson RB. Opportunities and barriers to pumped-hydro energy storage in the United States. Renewable and Sustainable Energy Reviews 2011;15:839–44.
[17] Deane JP, Gallachoir BPO, McKeogh EJ. Techno-economic review of existing and new pumped hydro energy storage plant. Renewable and Sustainable Energy Reviews 2010;14(4):1293–302.
[18] Connolly D, Lund H, Finn P, Mathiesen PBV, Leahy M. Practical operation strategies for pumped hydroelectric energy storage (PHES) utilising electricity price arbitrage. Energy Policy 2011;39:4189–96.
[19] Bradshaw DT. Pumped hydroelectric storage (PHS) and compressed air energy storage (CAES). In: IEEE PES meeting energy storage, Seattle, WA; 2000.
[20] Crotogino F, Mohmeyer KU, Scharf R. Huntorf CAES: More than 20 years of successful operation, SMRI Spring Meeting; 2001, Orlando, FL, p. 351–357; Apr. 23–24, 2001.
[21] Crotogino F, Leonhard W. Compressed air storage-gas turbines-power plants to balance fluctuating wind energy production. DGMK Tagungsbericht 2004;2:431–8.
[22] Grazzini G, Milazzo A. A thermodynamic analysis of multistage adiabatic CAES. Proceedings of the IEEE 2012;100(2):461–72.
[23] Wang SY, Yu JL. Optimal sizing of the CAES system in a power system with high wind power penetration. Electrical Power and Energy Systems 2012;37:117–25.
[24] Madlener R, Latz J. Economics of centralized and decentralized compressed air energy storage for enhanced grid integration of wind power. Applied Energy 2013;101:299–309.
[25] Oró E, Gil A, de Garcia A, Boer D, Cabeza FF. Comparative life cycle assessment of thermal energy storage systems for solar power plants. Renewable Energy 2012;44:166–73.
[26] Bertolini E. JET design, construction and performance. Nuclear Energy 1990;29(1):31–45.
[27] Lazarewicz ML, Ryan TM. Integration of flywheel-based energy storage for frequency regulation in deregulated markets, IEEE PES general meeting, PES 2010, art. no. 5589748, 2010.
[28] Wolsky AM. The status and prospects for flywheels and SMES that incorporate HTS. Physica C: Superconductivity 2002;372–376:1495–9.
[29] Rummel T, Risse K, Ehrke G, Rummel K, Jhon A, Mönnich T, Buscher KP, Fietz WH, Heller R, Neubauer O, Panin A. The superconducting magnet system of the Stellarator Wendelstein 7-X. IEEE Transactions on Plasma Science. 2012;40(3):769–76.
[30] Mitchell N, Bessette D, Gallix R, Jong C, Knaster J, Libeyre P, Sborchia C, Simon F. The ITER magnet system. IEEE Transactions on Applied Superconductivity 2008;18(2):435–40.
[31] Sander M, Gehring R, Neumann H. LIQHYSMES—a 48GJ toroidal MgB2-SMES for buffering minute and second fluctuations. IEEE Transactions on Applied Superconductivity 2013;23(3).
[32] Green M, Strauss B. The cost of superconducting magnets as a function of stored energy and design magnetic induction times the field volume. IEEE Transactions on Applied Superconductivity 2008;18(2):248–51.
[33] Nomura S, Shintomi T, Akita S, Nitta T, Shimada R, Meguro S. Technical and cost evaluation on SMES for electric power compensation. IEEE Transactions on Applied Superconductivity 2010;20(3):1373–8.
[34] Sharma P, Bhatti TS. A review on electrochemical double-layer capacitors. Energy Conversion and Management 2010;51(12):2901–12.
[35] Li B, Pan X, He YB, Du H. Study of EDLC and its usage in stand-alone photovoltaic system. Advanced Material Research 2011;335-336:1368–75.
[36] Sahay K, Dwivedi B. Supercapacitors energy storage system for power quality improvement: an overview. Journal of Electrical Systems 2009:1–8.
[37] Dunn B, Kamath H, Tarascon J. Electrical energy storage for the grid: a battery of choices. Science 2011;334:928–35.
[38] Yang Z, Zhang J, Kintner-Meyer MCW, Lu X, Choi D, Lemmon JP, Liu J. Electrochemical Energy Storage for Green Grid. Chemical Reviews 2011;111:3577–613.
[39] Shigematsu T. Redox flow batteries for energy storage. SEI Technical Review 2011;73:4–13.
[40] Ponce de León C, Frías-Ferrer A, González-García J, Szánto DA, Walsh FC. Redox flow cells for energy conversions. Journal of Power Sources 2006;160:716–32.
[41] Weber Z, Mench MM, Meyers JP, Ross PN, Gostick JT, Liu Q. Redox flow batteries: a review. Journal of Applied Electrochemistry 2011;41:1137–64.
[42] Skyllas-Kazacos M, Chakrabarti MH, Hajimolana SA, Mjalli FS, Saleem M. Progress in flow battery research and development. Journal of the Electrochemical Society 2011;158(8):R55–79.

[43] Xiong B, Zhao J, Tseng KJ, Skyllas-Kazacos M, Lim TM, Zhang Y. Thermal hydraulic behavior and efficiency analysis of an all-vanadium redox flow battery. Journal of Power Sources 2013;242:314–24.
[44] Bartolozzi M. Development of redox flow batteries. A historical bibliography. Journal of Power Sources 1989;27:219–34.
[45] Thaller LH. Electrically rechargeable redox flow cells NASA TM X-71540, Lewis Research Centre, 1-5, 1974.
[46] Thaller LH. Performance mapping studies in redox flow cells NASA TM X-82707, Lewis Research Centre, 1-6, 1974.
[47] Giner J, Swette L, Cahill K. Screening of redox couples and electrode materials NASA CR-134705, Lewis Research Centre, 1-107, 1976.
[48] Reid M, Gahn R. Factors affecting the open-circuit voltage and electrode kinetics of some Iron/Titanium redox Flow Cells NASA-TM-X-73669, Lewis Research Centre, 1-11, 1977.
[49] Thaller LH. Redox flow cell energy storage system NASA TM-79143, Lewis Research Centre, 1-8, 1979.
[50] Hagedorn NH. NASA redox storage system development project final report DOE/NASA/12726-24, NASA TM-83677, Lewis Research Centre; 1984.
[51] Tanaka T, Sakamoto T, Mori N, Mizunami K, Shigematsu T. Development of a redox flow battery. SEI Technical Review 1990;137:191.
[52] Sun B, Skyllas-Kazacos M. A Study of the V(II)/V(III) redox couple for redox cell application. Journal of Power Sources 1985;15:179–90.
[53] Sun B, Rychik M, Skyllas-Kazacos M. Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery. Journal of Power Sources 1985;16:85–95.
[54] Rychik M, Skyllas-Kazacos M. Characteristics of a new all vanadium redox flow battery. Journal of Power Sources 1988;22:59–67.
[55] Dawe J. Flow battery storage applications with wind power, Paper 05GM0535. In: IEEE PES GM conference, San Francisco; June 14 2005.
[56] Shigematsu T, Kumamoto T, Deguchi H, Hara T. Applications of a vanadium redox-flow battery to maintain power quality. In: Transmission and distribution conference and exhibition 2002: Asia Pacific, IEEE/PES, 2, 1065–1070, 2002.
[57] Menictas C, Skyllas-Kazacos M. Performance of vanadium-oxigen redox fuel cell. Journal of Applied Electrochemistry 2011;41:1223–32.
[58] Skyllas-Kazacos M, Kazacos G, Poon G, Verseema H. Recent advances with UNSW vanadium-based redox flow batteries. International Journal of Energy Research 2010;34:182–9.
[59] Kaneko H, Negishi A, Nozaki K, Sato K, Nakajima M. Redox battery, US Patent 5318865; 1992.
[60] Menictas C, Skyllas-Kazacos M. Vanadium–oxygen redox fuel cell, final report. SERDF Grant, NSW Department of Energy; 1997.
[61] Shibata A, Sato K. Development of vanadium redox flow battery for electricity storage. Power Engineering Journal 1999;13(3):130–5.
[62] J McDowell. International renewable energy storage conference, IRES2006, Gelsenkirchen, Germany; 30–31 October 2006.
[63] Huang KL, Li XL, Liu SQ, Tan N, Chen LQ. Research progress of vanadium redox flow battery for energy storage in China. Renewable Energy 2008;33:186–92.
[64] Müller B. Electricity on tap Fraunhofer magazine 1.10, Energy, 14-15, 2010.
[65] Parasuraman A, Lim TM, Menictas C, Skyllas-Kazacos M. Review of material research and development for vanadium redox flow battery applications. Electrochimica Acta 2013;101:27–40.
[66] Sun CN, Delnick FM, Aaron DS, Papandrew AB, Mench MM, Zawodzinski TA. Probing electrode losses in all-vanadium redox flow batteries with impedance spectroscopy. ECS Electrochemistry Letters 2013;2(5):A43–5.
[67] Aaron D, Sun CN, Bright M, Papandrew AB, Mench MM, Zawodzinski TA. In situ kinetics studies in all-vanadium redox flow batteries. ECS Electrochemistry Letters 2013;2(3):A29–31.
[68] Manahan MP, Liu QH, Gross ML, Mench MM. Carbon nanoporous layer for reaction location management and performance enhancement in all-vanadium redox flow batteries. Journal of Power Sources 2013;222:498–502.
[69] Gonzalez Z, Vizireanu S, Dinescu G, Blanco C, Santamaría R. Carbon nanowalls thin films as nanostructured electrode materials in vanadium redoxflowbatteries. Nano Energy 2012;1:833–9.
[70] Aaron DS, Liu Q, Tang Z, Grim GM, Papandrew AB, Turhan A, Zawodzinski TA, Mench MM. Dramatic performance gains in vanadium redox flow batteries through modified cell architecture. Journal of Power Sources 2012;206:450–3.
[71] Jia C, Liu J, Yan C. A significantly improved membrane for vanadium redox flow battery. Journal of Power Sources 2010;195:4380–3.
[72] Li X, Zhang H, Mai Z, Zhang H, Vankelecom I. Ion exchange membranes for vanadium redox flow battery (VRB) applications. Energy & Environmental Science 2011;4:1147–60.
[73] Hickner Michael A. Water-mediated transport in ion-containing polymers. Journal of Polymer Science Part B: Polymer Physics 2012;50:9–20.
[74] Di Noto V, Guarnieri M, Moro F. A dynamic circuit model of a small direct methanol fuel cell for portable electronic devices. IEEE Transactions on Industrial Electronics 2010;57(6):1865–73.
[75] Ma X, Zhang H, Xing F. A three-dimensional model for negative half cell of the vanadium redox flow battery. Electrochimica Acta 2011;58:238–46.
[76] Tang A, McCann J, Bao J, Skyllas-Kazacos M. Investigation of the effect of shunt current on battery efficiency and stack temperature in vanadium redox flow battery. Journal of Power Sources 2013;242:349–56.
[77] Alotto P, Guarnieri M, Moro F, Stella A. A proper generalized decomposition approach for fuel cell polymeric membrane modelling. IEEE Transactions on Magnetics 2011;47(5):1462–5.
[78] Alotto P, Guarnieri M, Moro F, Stella A. Multi-physic 3D dynamic modelling of polymer membranes with a proper generalized decomposition model reduction approach. Electrochimica Acta 2011;57:250–6.
[79] Skyllas-Kazacos M, Kazacos M. State of charge monitoring methods for vanadium redox flow battery control. Journal of Power Sources 2011;196:8822–7.
[80] Vazquez S, Lukic SM, Galvan E, Franquelo LG, Carrasco JM. Energy Storage Systems for Transport and Grid Applications. IEEE Transactions on Industrial Electronics 2010;57(12):3881–95.